# III.B.3 Fundamental Reforming Studies - Role of Catalytic $O_2$ Supports on Fuel Reforming

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## Objectives

- Search for long-duration reforming catalysts in the development of auxiliary power units.
- Investigate the role of oxygen-conducting supports in reforming of diesel fuel compounds and their role in decreasing carbon formation and/or increasing sulfur tolerance.

## Approach

- Several sample matrices of ceria-based catalysts will be studied to elucidate the effects of the following variables on the rate of carbon formation and conversion:
  - Support type ($CeO_2$ and $Al_2O_3$)
  - Catalyst type (Pt, Ni, Rh)
  - Dopant concentration in the oxygen ion conductor
  - Dopant type (La, Gd) in the oxygen ion conductor
  - Ionic conductivity
  - Oxygen storage capacity vs. ionic conductivity
- Catalyst characterization will include ionic conductivity, oxygen storage capacity, surface area, dispersion, crystal size, crystal phase and surface composition.
- Catalytic activity and selectivity will be determined for partial oxidation of hydrocarbons (POH) as a function of temperature, $CH_4/O_2$ and space velocity.
- Post reaction analysis of the catalysts will include transmission electron microscopy (TEM) and/or scanning electron microscopy (SEM), surface area, crystal size and crystal phase.
- Labeled reaction mixtures and labeled doped ceria catalysts will be tested during isotopic studies.
- Post reaction analysis by nuclear reaction analysis and secondary ion mass spectroscopy is planned to complement the isotopic studies.
- Studies related to sulfur tolerance are planned for the second stage of this project.

## Accomplishments

- Experimental facilities were constructed, including two catalytic flow reactors conditioned to operate with liquid fuels and liquid products, mass spectrometer and Auto Chem 2910 analytical instruments.
- A comprehensive test matrix was developed to examine most relevant variables.
- Catalytic experimental tests and catalyst characterization have been initiated.
- Partial oxidation of methane was conducted on $Rh/Al_2O_3$ as a function of temperature.

- Catalytic activity of $Pt/CeO_2$ during partial oxidation of methane was examined.
- Surface area of catalysts was determined, and results showed values in the range of 30-60 $m^2/g$.
- A review paper was presented at the Second International Conference on Fuel Cell Science, Engineering and Technology.
- Merit review was presented.

### Future Directions

- Study the role of oxygen-conducting supports to increase sulfur tolerance.
- Investigate the effects of supported metal alloys and their role in decreasing carbon deposition and/or increasing sulfur tolerance.
- Further investigate catalysts that are able to mitigate carbon formation and or increase sulfur tolerance.

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## Introduction

Ceria-based catalysts are being investigated in order to fundamentally understand the role of oxygen-conducting supports in reforming of diesel fuel compounds and their role in decreasing carbon deposition. Ceria-based catalysts have shown ability to decrease carbon formation during partial oxidation of hydrocarbons (1,2). It has been speculated that this property is due to their high oxygen ion mobility. In this project, this assumption will be further investigated. This project is in an early stage, and most of the work conducted so far includes the set-up of experimental facilities and elaboration of experimental plan.

## Approach

Ceria-based catalysts will be investigated, and the amount of deposited carbon will be determined as function of support type ($CeO_2$ and $Al_2O_3$), catalyst type (Pt, Ni, Rh), dopant type (La, Gd), dopant concentration, ionic conductivity and oxygen storage capacity. Catalytic activity and selectivity as a function of temperature, $CH_4/O_2$ and space velocity will be determined during the POH reactions.

Characterization of ceria-based catalysts will include ionic conductivity, oxygen storage capacity, surface area, dispersion, crystal size, crystal phase and surface composition. Post reaction analysis will include surface area and particle size, and selected samples will be analyzed by SEM to investigate types of carbon.

Isotopic exchange studies will be performed in order to obtain a mechanistic understanding of the influence of the oxygen ion mobility on the mitigation of carbon formation. Labeled reaction mixtures and doped ceria catalysts will be used in these experiments. Post reaction analysis of the catalysts by nuclear reaction analysis and secondary ion mass spectroscopy will allow quantifying the role of lattice oxygen in the formation of carbon.

## Results

Table 1 shows product composition as a function of temperature for the partial oxidation of methane on $Rh/Al_2O_3$. The reaction was conducted at $CH_4/O_2$=2 and space velocity = 60,000 $cm^3h^{-1}g^{-1}$. The catalytic activity tests were performed at different temperatures ranging from 450ºC to 850ºC, and catalysts were kept for 1 hour at each temperature. The conversion of methane and the production of CO and $H_2$ are increasing as a function of temperature. The concentration of $CO_2$ is higher at lower temperatures and lower at higher temperatures. This

**Table 1.** Partial Oxidation of Methane over $Rh/Al_2O_3$ (60,000 $cm^3h^{-1}g^{-1}$)

| Mol (%) | 450ºC | 550ºC | 650ºC | 750ºC | 800ºC | 850ºC |
|---|---|---|---|---|---|---|
| $CH_4$ | 6.68 | 5.15 | 3.22 | 2.09 | 1.25 | 0.74 |
| CO | 0.51 | 3.00 | 5.44 | 6.90 | 7.95 | 8.67 |
| $CO_2$ | 3.25 | 2.34 | 1.25 | 0.68 | 0.33 | 0.07 |
| $H_2$ | 4.90 | 8.95 | 12.21 | 14.59 | 16.36 | 17.52 |

agrees with the reaction mechanism proposed for the partial oxidation of methane. It is suggested that it occurs in two steps: in the first step, combustion of methane takes place, producing $CO_2$ and $H_2O$; in the second step, synthesis gas is produced via $CO_2$ and steam reforming reactions of un-reacted methane. It is also suggested that the $CO_2$ reaction is slower than the steam reforming, which explains the higher concentrations of $CO_2$ at lower temperature (3).

Table 2 shows the product composition for thepartial oxidation of methane, conducted on Rh/$CeO_2$ at 850ºC for 5 hours, space velocity = 21,000 $cm^3h^{-1}g^{-1}$ and $CH_4/O_2$=2.

**Table 2.** Partial Oxidation of Methane over Pt/$CeO_2$ at 850ºC (21,000 $cm^3h^{-1}g^{-1}$)

| Compound | Mol (%) |
|---|---|
| $CH_4$ | 1.92 |
| CO | 8.44 |
| $CO_2$ | 0.16 |
| $H_2$ | 17.21 |

## Conclusions

This project has just recently started and it is in an early stage. Although it is too early to quantify, limited testing of ionically conductive supported catalyts shows a trend towards less carbon formation than is observed in non-conductive supported catalysts.

## References

1. Applied Catalysis A: General 225(2002) 63-75.
2. Applied Catalysis B: Environmental 19 (1998) 267.
3. Catalysis Letters Vol. 91, Nos. 1 2 November 2003.

## FY 2004 Publications

1. "Synthesis gas by partial oxidation and the role of oxygen-conducting supports: A review" was accepted for publication as proceedings from the Second International Conference on Fuel Cell Science, Engineering and Technology (2004).

## FY 2004 Presentations

1. Presentation at the Second International Conference on Fuel Cell Science, Engineering and Technology. June 16, 2004. "Synthesis gas by partial oxidation and the role of oxygen-conducting supports: A review".